

Bioturbation-Driven Transport of Hydrophobic Organic Contaminants from Bed Sediment

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ABSTRACT

Compared to molecular diffusion the bioturbation-driven soluble fraction transport for hydrophobic organic chemicals (HOCs) from bed sediment is rapid, and it increases with increasing partitioning on the particle phase. This behavior is supported by three sets of data: one is PCB from the Hudson River, NY, and the other two sets are PAHs and chlorinated benzenes in laboratory microcosms. The proposed mechanisms for this behavior are: (1) bioturbation of particle-bound HOCs from depth through the upper decimeter of the bed to the interface, (2) rapid chemical desorption at the sediment–water interface followed by (3) transport through the benthic boundary layer to the water column. Based on this mechanism, a simple transport equation is developed, then used to correlate the data and extract intrinsic transport coefficients. These in-bed particle biodiffusivities and benthic boundary layer coefficients are comparable to other reported measurements.

Key words: bioturbation-driven transport; hydrophobic organic contaminants; bed sediment

INTRODUCTION

CHEMICAL FATE AND TRANSPORT (CFaT) modeling studies of the natural recovery processes in contaminated sediment beds are performed prior to selecting a remediation technique. Such activities are presently underway on the Hudson and Grasse Rivers in New York, and the Fox River in Wisconsin to name a few. These models are based on physical, chemical, and biological processes, and are designed to predict future levels of chemical concentrations in the bed, water column, and

fish. Subsequently, the models are used in further feasibility studies to help evaluate and compare the effectiveness of various clean-up techniques such dredging, *in situ* capping, augmented *in situ* bioremediation, and other techniques. Algorithms based on theoretically sound bed-to-water column transport processes supported by high-quality laboratory and field measurements are necessary if these models predictions are to be viewed with confidence. Increasingly, users are finding the need to use “calibrated” transport rate coefficients, larger than molecular diffusion-based ones, and unrelated to particle resuspension.

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sion in CFaT models to account for the sizable quantities of chemical released between storm events (Blasland, 1999; Limno-Tech, 1999; QEA, 1999; U.S. EPA, 2000). These soluble releases from the beds during low-flow periods are very significant; projected to be 30% of the PCBs released in the Lower Fox River (Limno-Tech, 1999). Similarly, large coefficients were needed for PCBs on the Hudson River. In addition, it was observed that the coefficients increased with increased partitioning on sediment solids (U.S. EPA, 2000). The objectives of this paper are: (1) to present and summarize published material that reports large sediment-to-water transport coefficients related to increased partitioning, (2) propose a coupled bioturbation driven sediment and benthic boundary layer (BBL) chemical transport process and model as an explanation, and (3) to compare the intrinsic transport parameters extracted from the data with other published measurements.

The material that follows starts with a definition of terms and a presentation of the theoretical model including some key aspects of its behavior related to the bioturbation-chemical partitioning process. This is followed by a review of three published studies containing observations of larger-than-molecular diffusion solute transport coefficients for several hydrophobic organic chemicals (HOCs). Two involve laboratory microcosm measurements with worms as the sediment-bed bioturbators, and the third involves field measurements. New interpretations of the data will be presented and discussed. Following this, the coefficients will be summarized in tabular form; their magnitude and variabilities shown as a function of increasing HOC partitioning onto solid particles. Next, theoretical model predictions of the transport coefficients will be displayed graphically along with all the available data. Finally, intrinsic biodiffusion coefficients and BBL coefficients extracted from the combined data sets will be compared to other published values.

MODEL PRESENTATION AND THEORY

A recent review of the literature on the subject of bioturbation covers the early literature and the development of the models to describe the process in mathematical terms (Bosworth and Thibodeaux, 1990; Water Environmental Research, 1995). Several approaches including box models (Berner, 1980), nonlocal transport (Bordeaux, 1986), levy flight (Mohany, 1997), and Fickian diffusion formalisms (Guinasso and Schink, 1975) have been proposed to describe the process and quantify the important aspects. Although the nonlocal and levy flight theories mimic animal activities more closely, in prac-

tice, the Fickian diffusion approach dominates the area of model applications (Thibodeaux, 1996). This approach is supported by data on in-bed particle reworking profiles derived from radioisotope and other particle tracer studies interpreted with diffusion models (Water Environmental Research, 1995). In addition to being a particle redistribution process, bioturbation was extended to quantify the transport of soluble seabed minerals and nutrients (Aller, 1977). This was later followed by application to sparingly soluble organics pollutants where it was demonstrated that particle-bound PCBs behaved similarly (Thibodeaux *et al.*, 1990; Reible *et al.*, 1991). A resistance-in-series approach coupling the bedside bioturbation process to transport through the benthic boundary layer was developed and used (Thibodeaux *et al.*, 1990); later it was extended and generalized (Thibodeaux, 1996). It is well known that other bedside processes are active that do not depend on particle resuspension from the bed surface. These include solute molecular diffusion and advection, Brownian diffusion of colloid bound (i.e., DOC) HOC fractions and biodiffusion of porewater, which occurs in parallel with particle biodiffusion. Based on calculations ranking these and other processes in low-energy estuarine or riverine environments, bioturbation was found to dominant contaminant movement rates in the upper sediment layer (Reible *et al.*, 1991). The model to follow has bioturbation as the only active process within the bed. Particle-associated chemical deposition and resuspension across the sediment-water interface are not included in this model.

A single equation is given in this section to define the transport coefficient currently used in CFaT models, and to present the resistance-in-series algorithm. The equation is:

$$\left[\frac{N}{(C^* - C_w)} \right] = K_w = \frac{1}{\frac{1}{\beta} + \frac{h}{D_b K_d \rho_b}} \quad (1)$$

The group $[N/(C^* - C_w)]$ on the left defines the overall mass-transfer coefficient, K_w (cm/day), used to quantify the rate of the so-called "diffusive"-soluble chemical fraction from within the bed to the water column. It is the ratio of the flux from the bed, N (mg/cm²·d), and the concentration difference within porewater, C^* (mg/cm³) and in the water column, C_w (mg/cm³). Ideally, both C^* and C_w are the sum of the soluble plus colloidal bound fraction but, as a practical matter the latter usually contributes little to the total concentration in the porewater and $C^* \gg C_w$. The concentration in bed porewater, at depth h (cm) below the surface, is either measured or estimated based on the measured concentration on bed particles, C_p (mg/g). The right side of Equation (1) is the algorithm for the resistance-in-series transport process.

The transport process that moves chemicals from the bed to the water column are transient. They approach a steady-state process behavior only under special circumstances. If these special circumstances apply either in the field or in the laboratory, then Equation (1) is a good approximation. The quasi-steady-state (QSS) assumption or methodology has been proposed for the field situation (Valasaraj *et al.*, 1997). Because of the slowness of the combined transport process within sediment, large time scales of decades or more are involved in the pollutant release process. So that over short periods of time of months to years it is appropriate to think of the rate of contaminant loss as approximately constant, and to refer to the short-term average as the QSS flux. This also implies that over this same time period there is a nearly constant "supply" of contaminated sediment at depth. This allows C^* to be constant as well. In laboratory microcosms the process is similar, but the contaminant mass is less. During the start-up period of a microcosm the initial flux from the bed is high. Readily available material on the surface of the bed causes the high flux. Within a few days the flux attains lower values. After 10 days to 2 weeks the flux assumes a near constant value; however, over a month or more a very gradual decline is noted. The term QSS is appropriate for this later period. With simultaneous daily measurements of the flux and C^* , for example, during this period the steady-state assumption inherent in Equation (1) is closely approximated. Two laboratory studies and one field study that met such QSS assumptions as outlined above have been located. The

data from the three studies will be used to obtain observations of K_w , the overall mass-transfer coefficient.

Details of the derivation of the right side of Equation (1) appear elsewhere (see pp. 323 to 325 of (Thibodeaux, 1996)). Only the result is presented here. It represents the following three-step process: (1) sediment particles containing the sorbed HOC are transported upward from depth by the process of bioturbation and positioned at or very close to the bed surface–water interface, (2) desorption occurs with the HOC molecules transformed from a particle-bound state into solution at the interface conditions of concentration, and (3) finally, the HOC is transported through the water-side benthic boundary layer to the water column. Figure 1 illustrates the various sediment layers and the chemical pathway. The location of the processes (1), (2), and (3) given above are shown in the figure. The average depth of origin of the particles is h (cm). The biodiffusion coefficient representing particle diffusivity in the bed is D_b (cm^2/day); this parameter quantifies the HOC transport as well, because the HOC is presumed to be almost entirely sorbed to particles. Chemical desorption at the interface is assumed to be rapid, so that the local equilibrium assumption (LEA) applies and is quantified by K_d . The bulk dry density of the bed solids is ρ_b (g/cm^3). Finally, β (cm/day) is the water-side benthic boundary layer (BBL) mass transfer coefficient. This parameter regulates the rate the HOC moves by diffusion through the thin, slow-moving, gently stirred water layer that resides above the bed surface. The arrangement of terms in the denominator on the

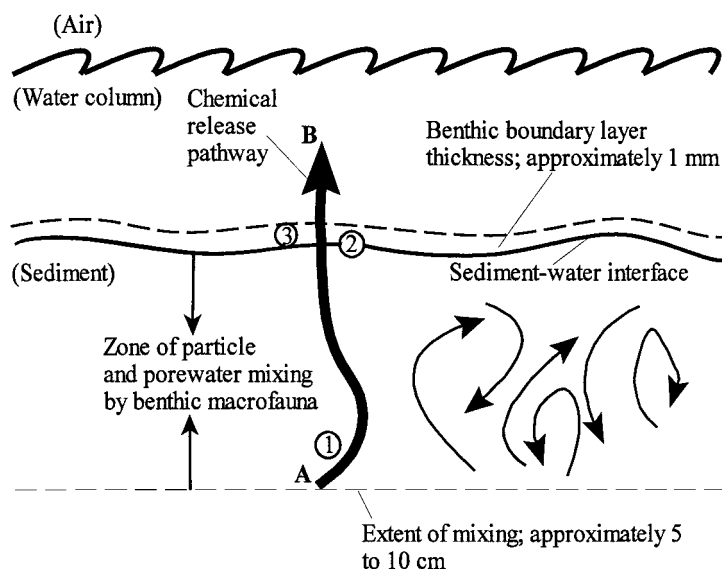


Figure 1. Illustration of the resistance-in-series process for soluble chemical release from bed sediment. The A and B denote the origin and terminus points of movement for the dissolved chemical fraction. The numbers 1 and 3 are keyed to the explanations of process mechanisms given in the text.

right side of Equation (1) is the algebraic expression for the resistance-in-series transport process.

In Equation (1) the product $D_b K_d$ regulates the HOC movement rate in the top 5 to 10 cm of the bed. D_b quantifies the particle conveyance rate to the surface, and K_d quantifies the relative chemical loading on the particles. HOCs with larger K_d s are, therefore, transported at higher rates. There are limits to this rate increase; however, an algebraic rearrangement of the right side of Equation (1) yields:

$$K_w = \frac{K_d}{[S + I \cdot K_d]} \quad (2)$$

This form of the model isolates the functionality of K_d in regulating the magnitude of K_w . The other parameters are contained in the defined constants: $S \equiv h/D_b \rho_b$ and $I = l/\beta$. In Equation (2), as K_d becomes large such that $I K_d \gg S$, then $K_w = 1/I$ or $K_w = \beta$. The overall mass transfer coefficient is equal to the BBL mass transfer coefficient. This means that although in-bed particle mixing may become very rapid and chemical availability at the surface is high, the rate of HOC "diffusive" movement through the BBL becomes the controlling process. So, for HOCs with very large K_d the numerical values of K_w plateau to constant values rather than continue to increase. The magnitude of β in rivers is governed primarily by the speed of water movement near the bottom

(Boudreau, 1996; Thibodeaux, 1996). On the other hand, for small values of K_d the $I K_d \ll S$ so that $K_w \approx K_d \cdot D_b \rho_b / h$. In this case, K_w is directly proportional to K_d . The above described theoretical behavior of K_w vs. K_d is illustrated by the two curved lines in Fig. 2.

LABORATORY MICROCOSM STUDIES

The material presented in this section describes two laboratory studies of bioturbation-enhanced HOC release from bed sediment. Data collected contrast the rates due to molecular diffusion and biodiffusion. Worms were used as the bioturbators, these being the most common benthic invertebrate known to alter sediment (Water Environment Research, 1995).

The release of pyrene, dibenzofuran, and phenanthrene from Bayou Manchac sediments was studied in our laboratory at Louisiana State University, Baton Rouge; the methods and results are reported elsewhere (Reible *et al.*, 1996). Tubificid oligochaete densities of 0, 6,700, and 26,000 individuals per m^2 were employed in microcosms operated with water in sheet-flow over a flat sediment bed, 75 cm^2 surface area, without particle resuspension. Water out flow was collected, and the chemical mass quantified to obtain the flux, N . The net bioturbation flux

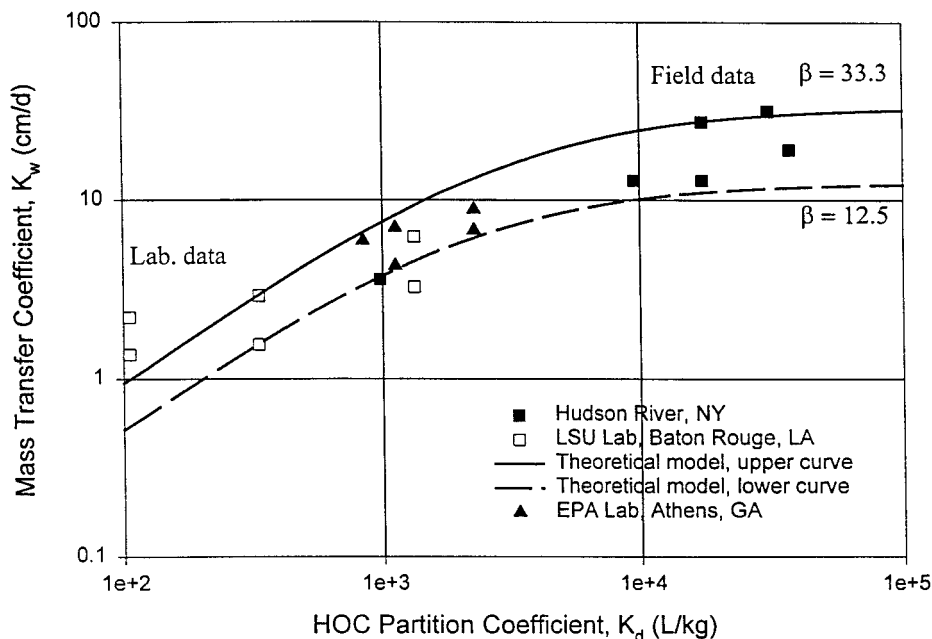


Figure 2. Soluble HOC sediment-to water transport coefficient. Coefficients for the release rate of HOCs as soluble material from sediment beds are displayed as a function of their partition coefficients. The triangle and open square symptoms are data from the laboratory microcosms experiments, and the dark square symbols are the field data. Dashed and solid lines are the theoretical model projections with parameters adjusted to bracket both the lab and field data sets.

was determined as the difference between the observed flux in the cells with worms and the control cells without worms. The data used were collected late in the experiment time period when the fluxes were very nearly constant so that the QSS assumption was applicable. Twelve microcosms were employed in each of the experiments, with four replicates at each biomass density including zero. Measured partition coefficients, K_d s and concentrations on sediment solids, C_p , were reported. The fraction organic carbon, f_{oc} , of the Bayou sediment was 0.021. In the original manuscript (Reible *et al.*, 1996), transport coefficients based on particulate HOC concentration were reported. In this paper they were transformed to equivalent K_w by Equation (1) $C^* = C_p/K_d$ and $C_w = 0$. The K_w values plus the partition coefficients appear in Table 1. The coefficient of variation (COVs) values were those reported for the flux measurements, N , in the microcosms. The objectives of the original manuscript was not to obtain observations on K_w nor to relate it to K_d as is shown in Table 1. Therefore, the present manuscript contains results obtained by reworking the original data toward a different objective.

At an earlier date laboratory microcosm studies were performed at the USEPA Environmental Research Laboratory Athens, GA, on the impact of tubificid oligochaetes for pollutant transport from bed sediments (Karickhoff and Morris, 1985). Hexachlorobenzene, pentachlorobenzene, and trifluralin were used on clean sediment from Culls Creek, GA, with tubificid worms harvested from the same site. The microcosms were 4-L flat-bottom glass bottles containing a sediment layer with worms and water column held at 15 to 20°C for 30 days. Air purging of the water without resuspending bed sediment maintained high dissolved oxygen and provided for the collection and measurement of test chemicals sparged from the water. Air-stripped chemicals were trapped on sorbent columns and

mass quantified to yield the flux, N , from the microcosms. Tubificid populations were maintained at the 10^4 to 10^5 individuals/m² level for the experimental period. Measured partition coefficients, K_d , and measured HOC concentrations on particles, C_p , were used to determine C^* . Use of the left side of Equation (1) yields K_w values, which appear in Table 2. The data presented in the original manuscript (Karickhoff and Morris, 1985) was measured fluxes for the three HOCs. Mass-transfer coefficients were not reported. Sufficient data on measured particle concentrations of HOCs at the beginning (i.e., day 0 to 10) and the end of the experimental period (i.e., day 20 to 30) was available in the original manuscript to allow estimates of K_w for these periods. The intent of the original manuscript was to evaluate the impact of worms on the pollutant flux from bed sediment. The present manuscript presents a reworking of the data contained in the original for results aimed at a different objective.

BIOTURBATION ENHANCED SOLUTE TRANSPORT

Both original manuscripts contained laboratory measurements comparing the molecular diffusion and bioturbation-driven transport processes for sparingly soluble chemicals released from bed sediment clearly shows the latter to be more rapid. With worm densities of 10^4 to 10^5 individuals/m² (>90% *Limnodrilus hoffmeisteri* and <10% *Tubifex tubifex*) hexachlorobenzene and pentachlorobenzene displayed a four- to sixfold increase over molecular diffusion in a 90-day period (Reible *et al.*, 1996). A similar enhancement was observed over a 48-day period in the laboratory for dibenzofuran, phenanthrene, and pyrene with the same type or organisms at a density of 2.7×10^4 individuals/m².

Table 1. LSU bayou manchac sediment—laboratory data

Chemical	Partition coeff. K_d (L/kg)	Mass-transfer coefficient	
		K_w (cm/day)	COV (%)
Medium density: 6700 ind./m ²			
Dibenzofuran	105	1.37	23
Phenanthrene	332	1.56	14
Pyrene	1325	3.27	26
High density: 26,700 ind./m ²			
Dibenzofuran	105	2.21	41
Phenanthrene	332	2.92	21
Pyrene	1325	6.23	18

Oligochaete worms in laboratory microcosm. Flux measured for each chemical. Measured particle-to-water partition coefficient. Equation (1) is used for mass transfer coefficient observation. COV = coefficient of variation.

Table 2. USEPA calls creek sediment—laboratory data

Chemical	Partition coeff. K_d (L/kg)	Mass-transfer coefficient	
		K_w (cm/day)	COV (%)
Early period; day 0 to 10			
Trifluarlin	840	5.91	—
Pentachlorobenzene	1120	7.00	2.6
Hexachlorobenzene	2240	8.85	4.9
Late period; day 20 to 30			
Trifluarlin	840	0.34	—
Pentachlorobenzene	1120	4.29	5.4
Hexachlorobenzene	2240	6.77	5.1

Oligochaete worms in laboratory microcosm. Flux measured for each chemical. Measured particle-to-water partition coefficient. Equation (1) is used for mass transfer coefficient observation. COV = coefficient of variation.

Calculations using theoretical models developed for both processes project even larger bioturbation-driven enhancements. The “characteristic” release times, defined as mass divided by rate, of trichlorophenyl for bed-sediment transport by molecular diffusion was 1,900 years and 10 years for bioturbation (Reible *et al.*, 1991). This is an enhancement of 190. Another comparison based on the effective molecular diffusion of A-1254, a PCB mixture, with $0.18 \text{ cm}^2/\text{year}$ vs. its observed biodiffusion coefficient in New Bedford Harbor sediment of $10 \text{ cm}^2/\text{year}$ yields a projected enhancement of nearly 60 (Thibodeaux *et al.*, 1990).

The disparity between the experimental and the theoretical model-derived enhancements is due to the effective time period of “measurement.” The experimental values typically reflect enhancements early on when molecular diffusion is highest. The models assume steady-state conditions when molecular diffusion is a very minor contributor. One group of investigators note that: “Initially, diffusion is dominant because contaminated sediment would be present at the sediment–water interface. Overtime, however, this region would become depleted of contamination and the rate of diffusion would slow. Bioturbation, however, would extend at least several centimeters into the sediment, and the rate would be maintained over long periods of time” (Reible *et al.*, 1996). At this juncture it should be appreciated that both theoretical approaches used above as examples of enhanced transport neglected the BBL contribution.

The laboratory observed enhanced flux behavior described above is reflected in the magnitude of the overall transport coefficients, K_w , shown for various HOCs in Tables 1 and 2. Taken altogether, the values span the range 0.3 to 9.0 cm/day. In contrast, solute molecular diffusion transport coefficients in porous sediment beds are much lower. Typically, the effective HOC diffusion co-

efficients in sediment pore spaces range from $7\text{E-}4$ to $7\text{E-}3 \text{ cm}^2/\text{day}$. Using a microcosm depth of 3 cm yields a K_w of 0.00024 to 0.0024 cm/day. A value of $K_w = 0.019 \text{ cm/day}$ was reported for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in molecular diffusion bed sediment (Valasaraj *et al.*, 1997).

A FIELD STUDY

A unique set of field data with published measurements on K_w has been located (U.S. EPA, 2000). It provides a huge contrast in the physical scale of transport under non-flow-generated particle resuspension conditions compared to the laboratory studies. What follows is a description of the site, details as to how the data was collected, and a summary of the published K_w results. The original data will be used in this manuscript as well, but evaluated and interpreted by using the proposed algorithm shown in Equation (2).

The Thompson Island Pool is a 6-mile portion of the Upper Hudson River, NY, containing a disproportionately large amount of the PCB mass. Additionally, it contains the highest concentrations, and has been extensively sampled from 1976 to present. As part of the ongoing studies the Pool was used as the site or quantifying the release of the PCBs under low flows conditions with little or no sediment resuspension (U.S. EPA, 2000). A flow-by-concentration mass balance across the Pool divided by the area of the surficial sediment yielded the flux from the bed, N . The effective overall mass-transfer coefficient was obtained exactly as shown in the left-hand side of Equation (1). The porewater concentration, C^* , was obtained from measured concentration on particles, C_p , and measured partition coefficients. It was found that C^* was much larger than C_w . Data on Tri^+ and five PCB

congeners were used. The Tri^+ represents the sum of only trichloro through decachloro homologues, and is a surrogate for total PCB in the sediments. The five congeners are: BZ#9 (a dichlorobiphenyl), BZ#28 (a tri-chlorobiphenyl), BZ#52 (a tetra-chlorobiphenyl), BZ#[90+101] and BZ#138 representing the coeluting penta-chloro and hexa-chloro biphenyls, respectively. The measured partition coefficients for bed sediments along with the measure mass transfer coefficients are shown in Table 3. Partition coefficients were temperature adjusted according to the water column temperature using an empirical relationship based on Hudson River data (U.S. EPA, 2000). The surficial bed-sediment temperature was assumed to closely track that of the water column. The average f_{oc} in sediment was 0.0182. The original K_w value, excluding Tri^+ , appear in Fig. 6-59 of the U.S. EPA (2000). They were obtained from data on 14 selected days for which measurements were available on all five. The Tri^+ mass transfer coefficients are the result of 140 individual observations of paired (same-day) concentration upstream at Ford Edward and downstream at the Thompson Island Dam; these appear in Fig. 6-54 of the U.S. EPA (2000). All measurements for evaluating K_w were under nonresuspending conditions in the Pool. No direct bioturbation evidence of particle mixing rates were available in the Upper Hudson River, nor is there any evidence to rule out advection from the bed. The investigators nevertheless point to bioturbation as one likely process for the nonflow-dependent PCB desorption to the water column. In addition, they report a seasonal pattern of K_w variation with distinctly higher values in the summer relative to most of the year. This behavior may be temperature-enhanced biological activity or rapid growth in organism numbers. Radionuclide and contaminant profile-derived particle mixing depth vary widely with values of 10 cm to greater than 20 cm in some locations. So, the evidence for bioturbation is circumstan-

tial. On the other hand, the absence of bioturbators in this stretch of the Hudson River would be an extremely unusual occurrence.

RESULTS AND DISCUSSION

Data from these studies supporting a relationship between K_w , the transport coefficient, and the sediment bed particle-to-water partition coefficient, K_d , appear in Tables 1 to 3 and in Fig. 2, graphed as K_w vs. K_d . The last column in the tables contains statistical data on the K_w . It should be noted that the laboratory-derived K_w values in Tables 1 and 2 are for long-term bioturbation; they do not reflect the transient, early-time aqueous diffusion time period. The flux data used for the K_w determination was obtained after the aqueous diffusion process had effectively ended. For the LSU Laboratory data (Table 1) the modest values of the coefficient of variation (COV) suggest significant overlap in K_w s for dibenzofuran (DIBZ) and phenanthrene (PHEN); however, the pyrene (PYR) values has little overlap with others. In Fig. 2, the K_w s of (PHEN) and (PYR), when connected with a straight line, have a slope of approximately unity. Theoretically, this behavior is expected for small K_d values according to Equation (2). The K_w of DIBZ deviates significantly from this behavior. With a K_d value equal 135 L/kg it displays a K_w much higher, being nearly equal to that of PHEN. With its relatively low K_d , much DIBZ exists in soluble form in the sediment porewaters, more so than the other two. It can be easily transported by molecular diffusion, biodiffusion of porewater and colloid (i.e., DOC) facilitated transport in addition to particle biodiffusion, thus elevating the flux and correspondingly the measured K_w . Calculated estimates of the first two processes suggest a 30% enhancement. The LSU Laboratory data shows an increase in K_w with an increase in worm population. Such behavior with D_{bs} has been documented to display a square root relationship with biomass density (Matisoff, 1982). For the U.S. EPA Laboratory data (Table 2) the range of K_d s representing trifluarilin (TFL), pentachlorobenzene (PCLB), and hexachlorobenzene (HCLB) is smaller than the previous set. With low COVs the K_w s of these substances show a clear pattern of increasing values with increasing K_d s. Because of the gradual but significant decline in the flux over the 30-day experimental period the Calls Creek data was divided into a 0–10-day time period and a 20–30-day time period. Measured concentrations on sediment, C_p , were available for these periods, and they meet the QSS criteria. Trifluarilin displayed significant microbial degradation, and as a result, only two measured values were obtained at the beginning and end. In addition, the

Table 3. Hudson River sediment—field data

PCB congeners	Partition coeff. K_d (L/kg)	Mass-transfer coefficient	
		K_w (cm/day)	COV (%)
BZ #4	977	3.6	42
Tri^+	9500	12.9	81
BZ #[90 + 101]	17,400	12.9	74
BZ #52	17,400	27.7	51
BZ #28	30,900	31.8	62
BZ #138	37,200	10.3	92

Flux from congener mass balance on Thompson Island pool and Equation (1) used to obtain mass transfer coefficient. Measured particle-to-water partition coefficient used. COV = coefficient of variation.

TFL K_w for the 20–30-day period was very low and does not appear in Fig. 2. Excluding it the graphical behavior of K_w vs. K_d appears nonlinear with a slope less than unity. According to Equation (2), this theoretical behavior is expected for $S = IK_d$ with K_d s in the mid-range region. For the Hudson River sediment (Table 3) there appears to be a trend of increasing K_w with increasing K_d s; however, the COV for K_w s are very large. Only the value for BZ#4 is arguably statistically different from the other five in the set. Likely the K_w s for the others are invariant with K_d and represent a constant value. Equation (2) predicts that K_w should be nearly constant at large K_d values. The K_d s in Table 3 are measured values, based on the ratio of particle to porewater concentrations from bed-sediment samples. It has been reported that the octanol–water partition coefficients of these chemicals increase with increasing congener numbers (Hawker and Connell, 1988). The K_d s for BZ#52 and BZ#28 deviate from this behavior, as can be seen in Table 3. Nevertheless, measured values are generally preferred over estimates of K_d . The values in the table are the measured ones; however, there appears to have been some sampling and procedural problems so that the accuracy of the measured K_d s is questionable (U.S. EPA, 2000, p. 102).

The authors of the Hudson River field study report that mass transfer coefficients for the five congeners and Tri⁺ were very different. A proposed model based on parallel particle plus porewater release without resuspension is used to obtain a relationship for the overall K_w (Batcher and Garvey, 1999; U.S. EPA, 2000). Model parameters were adjusted through congener pattern matching. They report that the approach gave reasonable results, however, did not completely explain differences in the sediment–water mass transfer between congeners (U.S. EPA, 2000, p. 119).

It is instructive to study the three sets of data as an ensemble. In doing so, S and I [see Equation (2)] values were selected and theoretical predictions made of K_w vs. K_d . For the upper curve $S = 102.5$ (L/kg)/(cm/day) and $I = 0.03$ (cm/day), while $S = 185$ and $I = 0.08$ for the lower. Excluding the DIBZ data for the reasons discussed previously, the curves displayed in Fig. 2 generally bracket the range of average K_w s and captures their behavioral trend with increasing K_d s. Because $\beta = 1/I$, the I s give $\beta = 33.3$ cm/day for the upper curve and 12.5 for the lower. These β s are within the range of values reported for rivers (Thibodeaux, 1996, p. 267). In addition, β is a strong function of water velocity (Boudreau, 1996, p. 183; Thibodeaux, 1996, p. 265), and it appears that the K_w s for the four congeners plus Tri⁺ varied considerably over the June 1995 to June 1997 period of observation (U.S. EPA, 2000). Part of their variation may reflect changes in water velocity in the Pool over the period. Al-

though the β s represented by the upper and lower theoretical curves are in line with field observations, none were reported for the individual laboratory microcosms studies. The average bioturbated depth, h , was 3 cm for both sets of laboratory data (Karickhoff and Morris, 1985; Reible *et al.*, 1996), and is estimated to be 5 cm for the field data (Boudreau, 1998). Solids concentration in the bed, ρ_B , ranged from 0.52 to 1.25 (g/cm) in the laboratory microcosms, and was measured at 1.25 in the field (U.S. EPA, 2000, Table 6-45). Using the definition of S [see Equation (2)], average values of D_b , the particle biodiffusion coefficient, can be estimated. Using $\rho_B = 1$ g/cm³, the range for the laboratory data is 0.016 to 0.030 cm²/day. For the tubificids worms in the Bayou Manchac sediment, the reported D_b s range from 0.0086 to 0.060 cm²/day (Reible *et al.*, 1996). For the Calls Creek sediment the investigators observed that the turnover time for fecal matter was the time required for the glass beads to reach the midpoint of the feeding zone, which varied from 30 to 70 days (Karickhoff and Morris, 1985). Using 1.5 cm as the midpoint of bead displacement, the average mean squared displacement is 1.125 cm². For the turnover times given, the glass bead D_b s are estimated to range from 0.016 to 0.038 cm²/day. For the field data with $\rho_B = 1.25$ g/cm², the theoretical curves in Fig. 2 represent D_b s 0.021 to 0.040 cm²/day. No bed-sediment particle mixing rates are available for the upper Hudson River; however, a value of 0.0027 cm²/day was estimated for Foundry Cove and Lents Cove in the Lower Hudson River (U.S. EPA, 2000). Values in the range of 0.014 to 0.083 cm²/day have been reported in waters of the northeast United States (Thibodeaux, 1996). In summary, it appears that the range of D_b s represented by the upper and lower theoretical curves of Fig. 2 are in general agreement with both the laboratory microcosm measurements and field observations.

CONCLUSIONS

A chemodynamic process model quantifying coupled transport and thermodynamic events on either side of the sediment–water interface is developed into a resistance-in-series algorithm for estimating mass transfer coefficients, K_w , of sparingly soluble chemicals released from the bed sediment. The algorithm is proposed for beds during flow time periods when little or no particle resuspension occurs. A reuse and analysis of published data from three studies is given to support the key predictions of the proposed model. The model predictions are that the transport coefficients are much larger than ones based on molecular diffusion and that K_d , the parameter that quantifies chemical partitioning, is the primary indepen-

dent variable controlling the magnitude of K_w . Reworking and reinterpreting the data of two laboratory studies with six HOCs provide the best evidence of K_w increasing with increasing K_d ; the original reports (Karickhoff and Morris, 1985; Reible *et al.*, 1996) did not draw this conclusion. Numerical values of biodiffusion coefficients, D_b , and water-side transport coefficients, β , extracted from the combined sets of laboratory and field data were consistent with other published observations and measurements. Taken as individual sets or in ensemble, the available data is consistent with the proposed resistance-in-series model. The field data collected on K_{ws} for the Hudson River reflecting PCB congeners with large K_d s appears invariant; however, the observations are highly variable and of questionable accuracy. Model predictions suggest that β , the benthic boundary layer coefficient regulates or controls the overall transport for mid-range to large K_d values. If further investigations support this prediction, then techniques need to be developed for measuring β s under field conditions.

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